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Synthesis of One-dimentional Nano-sized Defects in High T_c Superconductor

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14. ABSTRACT
This work showed that a high aspect ratio nano-scale hollow tube can be produced in a Y-Ba-Cu-O surface by focused ion beam (FIB) etching methods. However, production of matrices of deep hollow tubes on an individual basis would require long FIB operating times and would be costly. Cost and time limitations prevented the measuring of the superconducting properties of these materials.

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Abstract

It is known that flux pinning is optimized when the size of the defects approaches the superconducting coherence length (2–4nm for YBCO at 77 K), therefore, it is believed that nano-scale additions can be used to enhance the pinning as well as the superconducting critical current densities (J_c) at high temperatures (40-80 K) and high magnetic fields (1-10 Tesla or higher). Recent study by Haugan et al. showed that high defect densities up to 10^{11} nano-Y211 particles/cm^2 can be produced in multilayer Y211/Y123 films with significant higher J_c at high temperature and high field [1]. It is also known that the top-seeded melt-growth (TSMG) RE-Ba-Cu-O materials eliminate the detrimental weak link problem with single grain structures. A study by Murakami et al. shown that flux trapping capabilities up to 17 Tesla at 29 K in the TSMG Y-Ba-Cu-O superconductors can be achieved [2]. Such a high flux trapping property is important to large scale applications, e.g. superconducting motors, energy storage system, magnetic shields, etc.

Our recent studies of artificially adding nano-sized particles in the TSMG RE-Ba-Cu-O materials show significant enhancement of the J_c and pinning, especially at high magnetic field [3,4]. Nano-scale compositional fluctuation resulted from the additives were attributed to the enhancement of pinning. We also found that the characteristic of compositional fluctuation can be altered by the growth condition [5]. However, the feature of the compositional fluctuation is circular, i.e., it is isotropic. In this work, we propose to synthesize one-dimensional rod-like defects (or column-like defects) nano-sized second phase (RE211) in thick film RE-Ba-Cu-O superconductor.

If these processes were successfully developed, the pre-designed orientation with varied nano-rod or nano-whisker defect density can be produced to further enhance the J_c on pre-designed orientation. It is believed that this non-superconducting nano-rod with orientation perpendicular to the current flow plane will be more effective in enhancing J_c(H,T) along *ab* plane than point-like defects. On the other hand, compositional variations result from the reaction between the additives and matrix will provide the high- field pinning at the same time.

1. Background and statement of problem.

The coherence length of RE-Ba-Cu-O (RE=rare earth) superconductor is in the range of nano-meter, therefore, it is believed that nano-scale additions can be used to enhance the pinning as well as the superconducting critical current densities (J_c) at high temperatures (40-80 K) and high magnetic fields (1-10 Tesla or higher). A study by Murakami et. al. shown that flux trapping capabilities up to 17 Tesla at 29 K in the TSMG Y-Ba-Cu-O superconductors can be achieved [2]. Such a high flux trapping property is important to large scale applications, e.g. superconducting motors, energy storage system, magnetic shields, etc.

It is known that flux pinning is optimized when the size of the defects approaches the superconducting coherence length (2–4nm for YBCO at 77 K). Our previous studies of artificially adding nano-sized particles in the TSMG RE-Ba-Cu-O materials show significant enhancement of the pinning especially at high magnetic field [3-6]. In addition, nano-scale compositional fluctuation regions in RE-Ba-Cu-O material were observed and exhibit a J_c peak effect at high fields (~ 2 T at 77K and ~ 4 T at 65K) as shown in Fig. 1. It is believed that this peak effect (an increase, in stead of decrease, of J_c as the magnetic field increases) can be accounted by the formation of nano-scale compositional fluctuation.

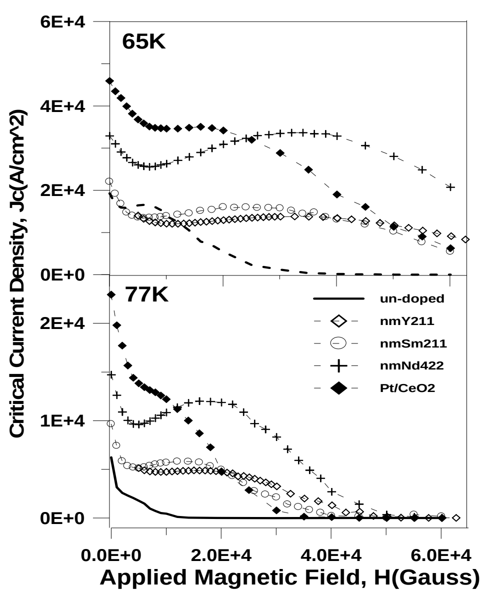
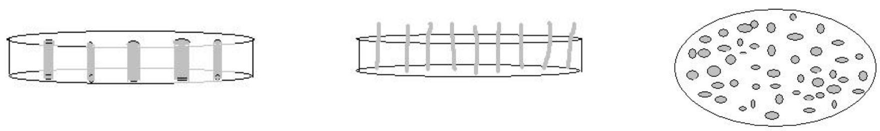


Fig. 1. J_c (H, T) H//c measurements at 77 and 65 K of TSMG SmBCO samples with different nano-particle, e.g. nano-Y211, nano-Sm211, nano-Nd422, additions.

Nevertheless, all these results are originated from point-like defects, not from one-dimensional rod-like defects (or column-like defects). In this work, we propose to synthesize one-dimensional nano-sized second phase defect in thick film RE-Ba-Cu-O superconductor as shown schematically in Fig.2. It is proposed that porous anodized aluminum oxide (AAO) structures will be grown on SrTiO3 single crystal substrate. The RE211 or other types of oxides will be grown to fill-in the pores by sol-gel process as shown in Fig. 2(a). The AAO will be dissolved with nano-rod-like RE211 left as shown in Fig. 2(b), the RE-Ba-Cu-O thick film will be grown over the RE211 and resulted in RE123/nano-rod RE211 composite structures as shown in Fig. 2(c).

If this process was successful developed, the pre-designed orientation with varied nano-rod or nano-whisker defect density can be produced to further enhance the J_c on pre-designed orientation at high temperature and high magnetic field. It is believed that this non-superconducting nano-rod with orientation perpendicular to the current flow plane will be more effective in enhancing $J_c(H,T)$ along a,b plane than point-like defects. These samples can also be used to test the theory of flux pinning in so-called an-isotropic (or 2 D) RE-Ba-Cu-O superconductors.



(a) (b) (c)

Fig. 2. Schematical illustration of the procedure to produce nano-sized second phase defect in thick film RE-Ba-Cu-O superconductor.

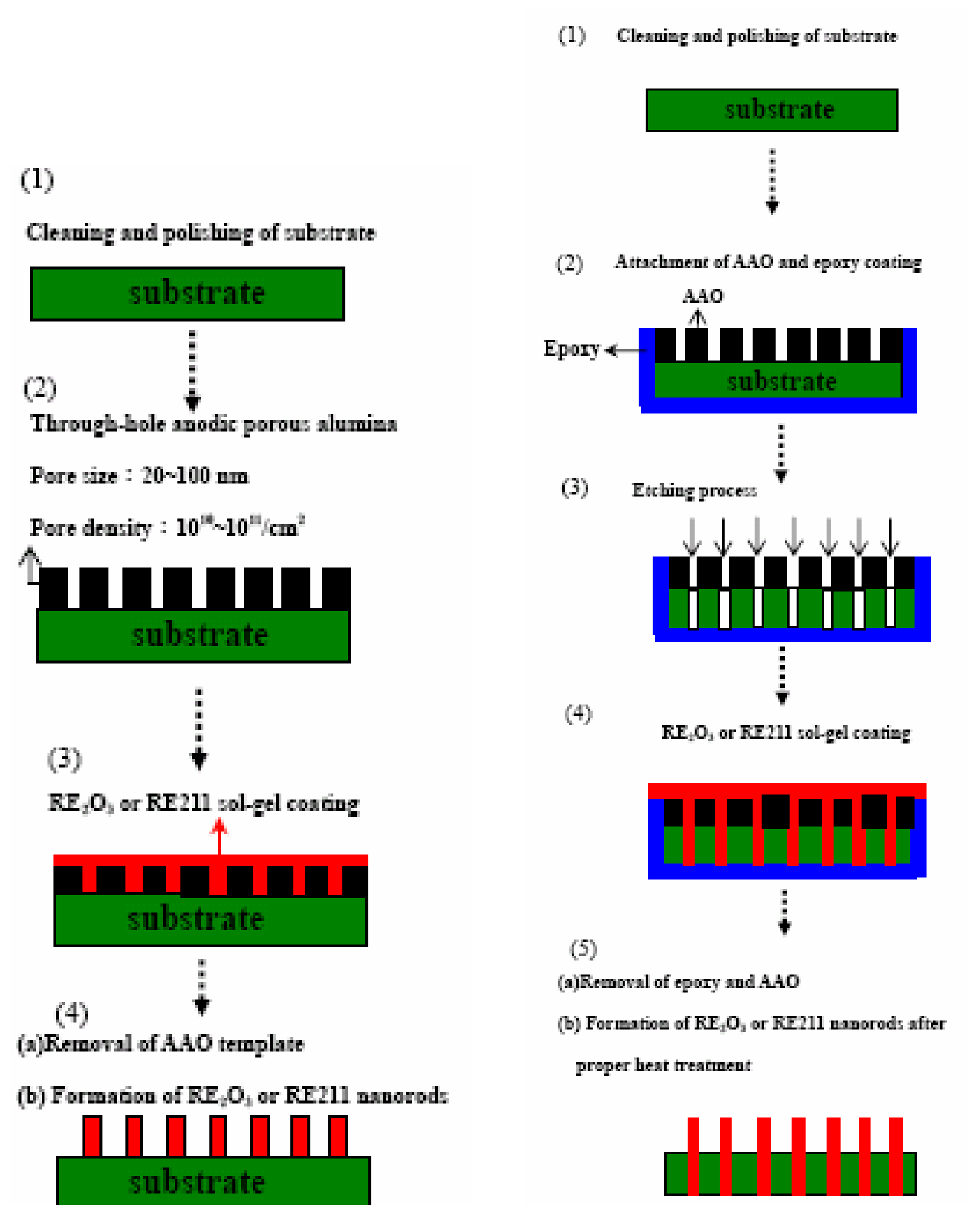
2. Proposed Approaches and Experimental Results

Two approaches have been proposed to solving this problem as shown in Fig. 3. The first approach is shown schematically in Fig. 3.a, the step-by-step procedure of the proposed study can be described as follows: (1) cleaning and polishing the TSMT Y-Ba-Cu-O superconductor surface, (2) attaching the AAO template (pore size ~ 20-100 nm, pore density ~ $10^{10} – 10^{11}$ /cm^2), (3) filling and produce RE-Ba-Cu-O 211 particles by sol gel + spin coating process, (4.a) removing AAO in alkaline solution, and (4.b) sintering and formation of RE-Ba-Cu-O 211 nano-rod or nano-whisker.

The second approach is shown schematically in Fig. 3.b, as follows: (1) cleaning and polishing the TSMT Y-Ba-Cu-O superconductor surface, (2) attaching the AAO template (pore size ~ 20-100 nm, pore density ~ $10^{10} – 10^{11}$ /cm^2) and encapsulate with epoxy, which will restrict the etching process, (3) the AAO template is used as a mask for the wet (or dry) etching process, (4) filling and produce RE-Ba-Cu-O 211 particles by sol gel + spin coating process, (5.a) removing AAO in alkaline solution, and (5.b) sintering and formation of RE-Ba-Cu-O 211 nano-rod or nano-whisker.

It is believed that nano-sized air/vacuum pore (which is an insulator) can act as pinning centers. Therefore, we have decided to conduct the 2nd approach to validate the feasibility of the processing methods. Both wet etching by different acid and dry etching by ionic bombardment method have been studied as shown in the following section.

Figure 4.a (pore size ~ 0.2μm) and 4.b (pore size ~ 0.02μm) show the SEM pictures of the 60μm thickness AAO templates (Whatman Co.) used as mask on Y-Ba-Cu-O single grain superconductors.



(a) (b)

Fig. 3. (a) Synthesis of RE211 nano-rod on AAO template, (b) Synthesis of RE211 nano-rod by etching off the substrate.

2. a. Wet Etching Approaches

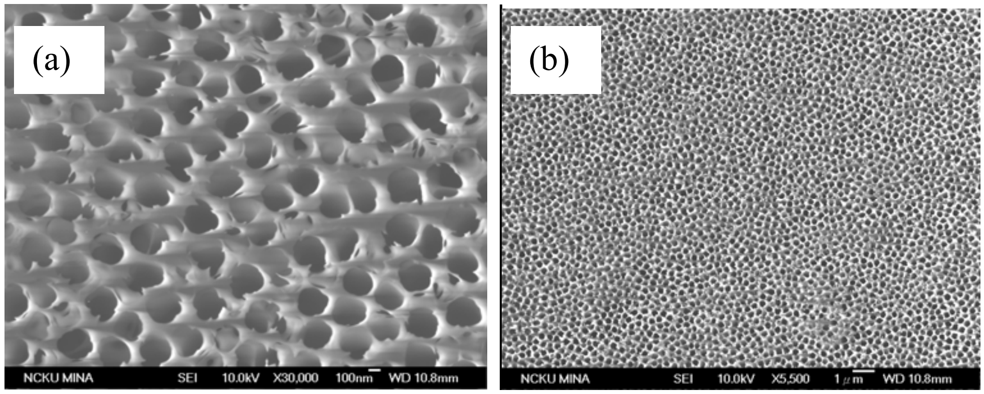


Figure 4. SEM pictures of the 60μm thickness AAO templates (Whatman Co.) (a)pore size ~ 0.2μm) and (b) pore size ~ 0.02μm used as mask on Y-Ba-Cu-O single grain superconductors.

Two different types of acids (5 M aqueous HCl and $HClO_4$) are used on the etching process. These two types of acids show moderate etching rate of Y-Ba-Cu-O and with insignificant etching rate of AAO. Two steps spin-coating process(1 st step□500 rpm□5 s, 2 nd step□1500rpm□15 s) is used to spread and penetrating acid into the 0.2μm pores of AAO. Figure 5 shows the SEM micrographs of the etched Y-Ba-Cu-O surface structures with AAO mask. It is shown that micro and sub-micro sized structure can be revealed by etching in the 5 M $HClO_4$ solution, which indicates that it is a potential technique to resolved in the fine structures (in the order of 100 nm) on Y-Ba-Cu-O. However, current process shows difficulty to ensure a close contact between the AAO template and polished Y-Ba-Cu-O surface. And a gap over a large area between AAO and Y-Ba-Cu-O will be formed that prevents the concept of using AAO as the mask to conduct the localized etching on Y-Ba-Cu-O. Unless the close contact problem can be resolved, dry etching method seems to be a more favored route to conduct localized etching experiment.

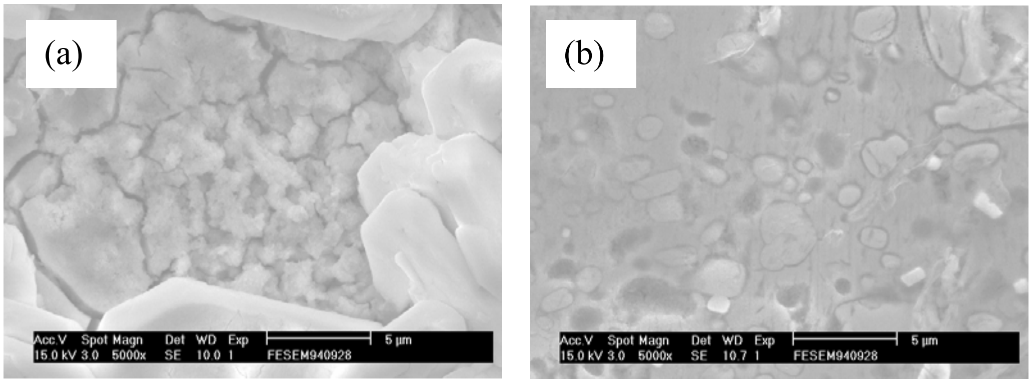
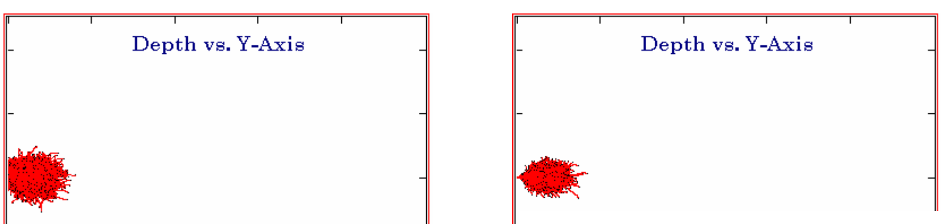


Fig. 5, SEM micrographs of Y-Ba-Cu-O etched surface (a) 5M HCl and (b) 5 M $HClO_4$ with 2 steps spin coating process.

2.b. Dry Etching Approaches

It is well known that high energy ion beam can transfer their kinetic energy to surface atoms, which will energize the surface atoms and ejected out of the surface. If these ejection of atoms were localized at nano-scale area, a column like of hollow tube in nano-scale will be created, which would become an effective pinning center. A focus ion beam (JEOL SMI-3050) with 30 KeV Ga+ ion source is used to conduct this feasibility study. The depth profile of the Ga+ ion bombardment on amorphous Y-Ba-Cu-O or AAO were simulated by TRIM computer program as shown in Fig. 6. The TRIM results show that nano-scale (<10 nm in lateral range) can be achieved by 30 KeV Ga+ ion source.

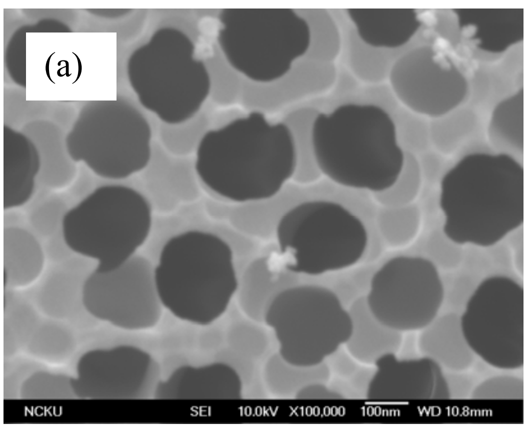


(a) amorphous Y-Ba-Cu-O
Longitudinal range: 25.7 nm
Lateral range : 8.5 nm

(b) amorphous AAO
Longitudinal range: 31.6 nm
Lateral range : 6.3 nm

Figure 6. TRIM simulation of (a) Y-Ba-Cu-O and (b) AAO bombarded by 30 KeV Ga + ion.

Figure 7.a and 7.b show the AAO surface before and after focus Ga + ion bombardment respectively. It is shown in 7.b that the opening diameter was reduced by in Fig. 7.b compared with that of Fig. 7.a. It is believed that the re-deposition of sputtered atoms on the top surface causes the reduction of the pore opening. This strong re-deposition effect of AAO mask will cause the etching of Y-Ba-Cu-O difficulty. A direct measurement of the etching rates (depth/dose) by JEOL SMI-3050 are 0.386 and 0.256 nm/ ion cm^2 for Y-Ba-Cu-O and AAO respectively.



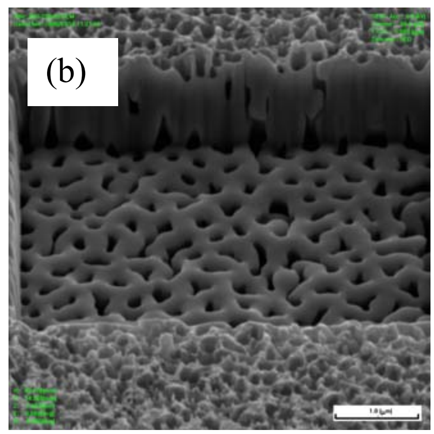


Fig. 7 a. AAO surface morphology (a) before and (b) after focused Ga + ion bombardment.

A different approach to create nano-size hollow tube in Y-Ba-Cu-O without the AAO mask has been studied by using the pixel mode of JEOL SMI-3050. Fig. 8(a) shows the pre-designed pattern (1 μm x 1μm lattice) of shallow etched Y-Ba-Cu-O surface. Each etching spot is about 50 nm diameter. Fig. 8(b) shows a single deep etched hollow tube (70 nm diameter x 570 nm depth) and Fig. 8(c) shows its dimensions. It is believed that with a further systematic studies on the FIB etching parameters, such as Ga + ion kinetic energy, flux density, beam diameter, will affect the etching rate as well as the aspect ratio of hollow-tube.

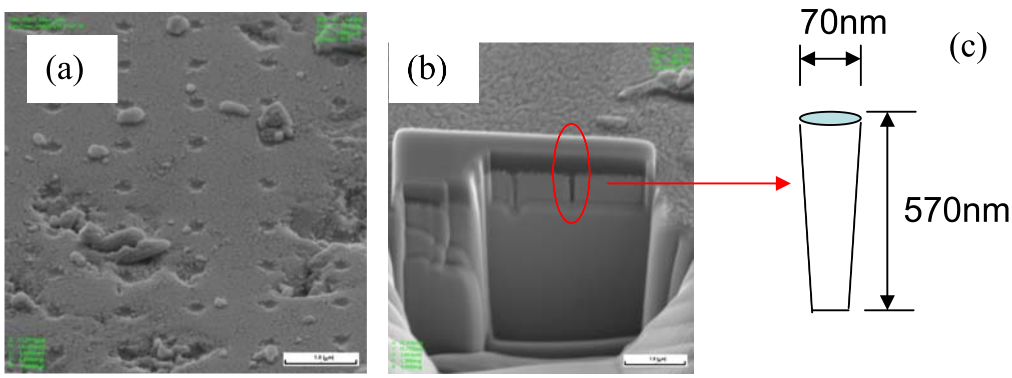


Figure 8 (a) 1 μm x 1μm lattice of shallow etched Y-Ba-Cu-O surface with each spot about 50 nm diameter, (b) FIB cross-section view of a single deep etched hollow tube, with its dimension shown in (c).

3. Summary of preliminary results and future works

These results indicate that high aspect ratio nano-scale hollow tube can be produced in Y-Ba-Cu-O surface by focused ion beam (FIB) etching methods. However, to produce a matrix of deep hollow tube one-by-one will consume a long operation time of FIB and high cost. Due to the limitation of the budget and time, no superconducting properties, such as critical transition temperature (Tc) and critical current density (Jc), has not been measured.

It has been designed to conduct a transport Tc and Jc measurement with about 10^5 nano-hollow-tubes in a 200 μm x 40 μm area as shown in Fig. 9. If all these hollow-tubes act as effective column pinning centers, a column defect density up to 10^9 cm^{-2} can be produced. This Y-Ba-Cu-O sample will also be measured in various temperatures and magnetic fields (applied in both c and ab orientations). If these processes were successfully developed, the pre-designed orientation with varied nano-rod or nano-whisker defect density can be produced to further enhance the J_c on pre-designed orientation. It is believed that this non-superconducting nano-rod with orientation perpendicular to the current flow plane will be more effective in enhancing $J_c(H,T)$ along *ab* plane than point-like defects.

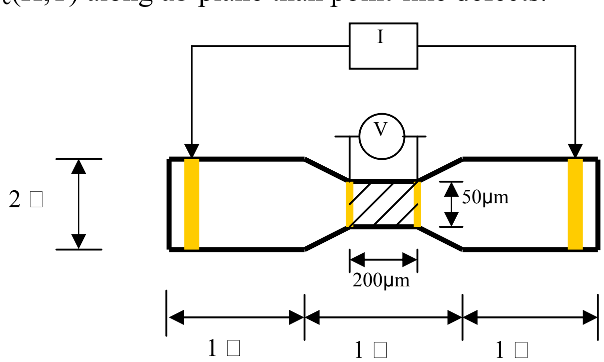


Fig. 9. Schematic sample diagram for transport Tc and Jc measurement. There are about 10^5 nano-hollow-tubes in a 200 μm x 40 μm area (shaded) which will be equivalent to a column defect density up to 10^9 cm^{-2}.

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